

or simultaneously with pneumatically assisted ES probes. Two or more pneumatic nebulization assisted ES probes configured with full tip position adjustment can be operated simultaneously in one ES chamber. Combinations of single, two layer and three layer ES probes can also be configured and operated simultaneously in a single ES chamber.

[0052] ES source 130, as diagrammed in FIG. 6, is configured with two ES probes with independent adjustable ES tip positions. Axis 124 of ES probe assembly 122 is positioned along ES source centerline 131 with ES probe tip 123 spaced a distance Z_1 along ES source centerline 131 from endplate nosepiece face 149. Axis 137 of ES probe assembly 120 is positioned at an angle of $\phi_{120}=70$ degrees relative to ES source centerline 131. Tip 121 of ES probe assembly 120 is shown located a distance Z_2 axially from end plate nosepiece face 149 and a distance r_2 radially from ES source centerline 131 with a radial angle $\theta_{120}=0$ degrees. Angle θ_i is defined as the radial angle around centerline 131 looking in the direction that the gas flows through the capillary or the positive z axis direction as shown in FIG. 1. The 12 o'clock position above centerline 131 is defined as 0 degrees with the angle increasing clockwise to 360 degrees. Setting $Z_1=2$ cm, $Z_2=1.5$ cm and $r_2=1.5$ cm, higher liquid flow rates can be introduced through ES probe tip 121 and lower liquid flow rates, with a solution containing calibration compounds, can be introduced through ES probe tip 123. Both ES probe tips 121 and 123 can be operated with pneumatic nebulization assist, for the tip positions and angles given. When higher liquid flow rates are sprayed from ES probe tip 123 the probe tip axis angle, ϕ_{122} , relative to ES source centerline 131 can be increased by turning adjustment knobs 125 and/or 126. Alternatively ES probe assembly 122 can be positioned off ES source centerline 131 but spraying approximately in a direction parallel to centerline 131. Depending on the specific analytical problem requiring ES MS analysis or ES MS/MSⁿ analysis, multiple ES probes can be positioned in the ES source to optimize performance for individual or simultaneous spraying operation.

[0053] Mass spectra acquired from a dual probe ES source configured similar to that shown in FIG. 6 are shown in FIGS. 7a through 7c. FIG. 7a shows a mass spectrum of a sample solution of 1:1 methanol:water containing Leucine Enkephalin Electrospayed with pneumatic nebulization assist at a liquid flow rate of 100 ul/min from ES probe tip 123 in dual probe ES source 130. Protonated m/z peak 153 of Leucine Enkephalin is the dominate peak in acquired mass spectrum 150. No solution was flowing through off axis probe ES probe tip 121 during acquisition of mass spectrum 150 shown in FIG. 7a. Mass spectrum 151 shown in FIG. 7b was acquired while a Electrospaying, with pneumatic nebulization assist, a calibration solution from ES probe tip 121 configured in dual probe ES source 130. The calibration solution contained known molecular weight compounds Tri-Tyrosine (50 pmol/ul) and Hexa-Tyrosine (50 pmol/ul) in an 80:20 solution of water:isopropanol with 2% propionic acid delivered from a sample reservoir at a flow rate of 5 ul/min. Calibration solution flow was driven primarily by the venturi force of the pneumatic nebulization gas flow at ES tip 121. Protonated molecular ions of Tri-Tyrosine 154 and Hexa-Tyrosine 155 are the primary peaks in mass spectrum 151. No solution was flowing through the ES probe tip 123 during acquisition of calibration spectrum 151 shown in FIG. 7b. FIG. 7c shows

mass spectrum 152 acquired while simultaneously spraying calibration and sample solutions from ES probe tips 121 and 123 respectively. Protonated molecular ion peaks 156 and 158 resulting from Electrospaying of the calibration solution can be used as an internal standard to improve the accuracy of the calculated mass assignment of the sample Leucine Enkephalin peak 157 or another unknown compound molecular weight. As was shown in FIGS. 4a through 4c, little signal loss is observed when comparing single and dual probe spraying. ES probe tip 121 and 123 positions were not changed during acquisition of the mass spectra 150, 151 and 152 shown in FIG. 7.

[0054] It is obvious to one skilled in the art that any number of combinations of multiple Electrospay probe tip positions may be configured in an Atmospheric Pressure Ion Source where:

[0055] 1. the Electrospay tip angles ($\phi_1, \phi_2, \dots \phi_N$) can range from $\phi_i=0^\circ$ to 180° ,

[0056] 2. the Electrospay tip locations (r_1, θ_1, z_1), (r_2, θ_2, z_2), (r_N, θ_N, z_N) can have values where r_i may equal any distance within the ES chamber, $\theta_i=0^\circ$ to 360° measured clockwise, and z_i may equal any distance within the ES chamber, and

[0057] 3. the relative Electrospay tip radial angle of separation ($\theta_1-\theta_2$), \dots ($\theta_1-\theta_N$) for any two ES probe tips i and k can range from $\theta_i-\theta_k=0^\circ$ to 360° ,

[0058] Electrospay probe assemblies may be configured with two or more parallel tips or with individual tips. ES probe tip positions may be adjustable or fixed in the ES chamber. Although FIGS. 1 and 6 show Electrospay sources configured with one off axis ES probe assembly, several off axis ES probe assemblies with different angles θ_i can be configured into an ES source chamber which may also include an ES probe assembly located near the ES source centerline. In addition, individual Electrospay probe tips may be configured with but not limited to any of the following ES tip types: a single layer Electrospay probe tip, a replaceable micro Electrospay tip, a flow through micro Electrospay tip, a pneumatic nebulization assisted Electrospay tip with or without liquid layer flow, an ultrasonic nebulizer assisted Electrospay tip or a heated Electrospay tip. Any combination of ES probe tip types can be configured into an ES source and operated individually or simultaneously. ES probes can be configured to extend through the wall of the ES chamber or be mounted entirely within the ES chamber.

[0059] FIG. 8 is a diagram of an alternative embodiment of the invention where three ES probes are configured within ES source 160. Electrospay source 160 includes cylindrical electrode 162 dielectric capillary 163, counter current drying gas 167, gas heater 168, endplate electrode 165 and attached endplate nosepiece 166. Alternatively, a non dielectric capillary, a heated capillary, a flat plate orifice or a nozzle can be configured as an orifice into vacuum replacing dielectric capillary 163. Multiple ES source probes can be configured with different arrangements of drying gas flow direction relative to the ES source axis and the axis of the orifice into vacuum such as those arrangements used with "z spray" or "pepperpot" Electrospay source geometries. ES probe assemblies 170, 171 and 172 are mounted in ES source chamber 161 each with x-y-z and angular position adjust-